

Inelastic light, neutron, and X-ray scatterings related to the heterogeneous elasticity of glasses

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Abstract

The effects of plasticization of poly(methyl methacrylate) glass on the boson peaks observed by Raman and neutron scattering are compared. In plasticized glass the cohesion heterogeneities are responsible for the neutron boson peak and partially for the Raman one, which is enhanced by the composition heterogeneities. Because the composition heterogeneities have a size similar to that of the cohesion ones and form quasiperiodic clusters, as observed by small angle X-ray scattering, it is inferred that the cohesion heterogeneities in a normal glass form nearly periodic arrangements too. Such structure at the nanometric scale explains the linear dispersion of the vibrational frequency versus the transfer momentum observed by inelastic X-ray scattering.

I. INTRODUCTION

The excess of low-frequency vibrational density of states (VDOS) in comparison with the Debye regime, called boson peak, is quasi-universal in glasses. It is generally admitted that its origin lies in nanometric fluctuations, its frequency being related to the correlation length. S. Elliott [1] interpreted the boson peak by density fluctuations which scatter and consequently localize the acoustic phonons, within a continuous random network, or a homogeneous structure (all points in the glass are considered as equivalent). More recently several authors interpreted the boson peak by atomic force or elastic constants fluctuations, still in homogeneous [2,3] structures.

As these interpretations show it, the excess of VDOS can be ascribed to fluctuations of density or of elastic constants within a homogeneous structure. In spite of that, several interpretations have postulated a heterogeneous glassy nanostructure to account for the fluctuations: in this case the correlation length corresponds to the heterogeneity size [4–7]. However, up to now, no clear density nanoheterogeneities have been observed by either small angle X-ray or neutron scattering, nor by electron microscopy. It is why the existence of cohesion heterogeneities was suggested [5]. Within this latter view, it is assumed that more cohesive nanodomains are separated by softer zones [8,9].

Several arguments, also based on the concept of heterogeneities though transient as they pertain to the liquid state, come as a strong support for the existence of cohesion heterogeneities within the glassy state. According to Stillinger, "the vitrifying liquid is viewed as a dynamic patchwork of relatively strongly bonded (but amorphous) molecular domains that are separated by irregular walls of weakened bonds" [10]. Such a description was confirmed, on the one hand by the multidimensional nuclear magnetic resonance technique, that made evident the existence of transient heterogeneities in the supercooled state [11], and on the other hand by simulation works that showed the existence of domains inside which atoms are more mobile [12]. Stillinger added "the mean domain diameter rises as temperature declines to minimize wall free energy, but the process is self-limiting due to intradomain frustration energy" [10]. Theories related to frustration, developed by Kivelson and Tarjus [13,14] do also predict a supermolecular heterogeneity termed as "frustration limited domains". From all these considerations, it appears natural that the so-called dynamical heterogeneities freeze upon cooling below the glass transition temperature, under the form of an inhomogeneous elastic constant network. An experimental evidence of the heterogeneous glass structure is found in a very recent paper [15], in which the heterogeneous molecular cooperative relaxation, at a temperature slightly lower than the glass transition, is experimentally demonstrated, by using a nanometric electric probe.

Very recently, numerical simulations using a Lennard-Jones potential, were able to confirm the existence of heterogeneities of elastic constants in disordered matter. Wittmer et al. [16] find that, in a 2-dimensional amorphous system, the atomic displacements become nonaffine with respect to the sample deformation below a length scale of 30 to 50 molecular sizes; these displacements are found to be correlated in regions of a size similar to this length scale. On the other hand, Viliani et al. [17], by determining the atomic potential energy variation induced by the normal vibrational modes, show that the correlation between "softest" atoms is at least as strong as in the whole sample. Such a heterogeneous elasticity is not far from the glass description by a heterogeneous distribution of positive and negative

internal stresses as suggested by Alexander [18] and simulated by Kustanovich and Olami [19].

In the first part of this paper, by comparing the boson peaks observed by respectively Raman and inelastic neutron scattering of a plasticized polymeric glass, the relation between the boson peak and an experimentally observed heterogeneous nanostructure will be established. In the second part, it will be emphasized that the linear dispersion of the vibrational frequency ν versus the momentum transfer Q , that is generally observed by inelastic X-ray scattering [20–22], does not necessarily prove the vibrational energy propagation and is in agreement with the heterogeneous glass cohesion at the nanometric scale [23].

II. RAMAN AND NEUTRON BOSON PEAKS OF PLASTICIZED POLY(METHYL METHACRYLATE)

Recently the low-frequency Raman scattering (LFRS) of glassy poly(methyl methacrylate) (PMMA) plasticized by 23 (mass)% of dibutyl phthalate (DBP) was studied. The plasticized PMMA will be symbolized by PMMA/DBP. It was observed an enhancement of the Raman boson peak compared with the one that is expected for PMMA/DBP (Figure-1) [24]. On the contrary, no enhancement of the VDOS in the spectral range of the boson peak was observed by inelastic neutron scattering (Figure-2). One can observe in Figure-2 that the VDOS calculated by addition of the PMMA and DBP VDOS in PMMA/DBP fits perfectly the experimental VDOS of the plasticized PMMA [25]. As far as the static structure is concerned, a correlation peak was detected with PMMA/DBP by small angle X-ray scattering (SAXS) at an exchanged momentum $Q \simeq 0.15 \text{ \AA}^{-1}$ [24]. Such a correlation peak is absent in pure PMMA. This momentum Q value corresponds to a period of about 40 \AA in a quasiperiodic network. The obtained period is close to that deduced from the position of the boson peak in PMMA, using a model of inhomogeneous nanostructure [26]. It is remarkable that similar observations were done with another polymeric glass: an enhancement of the boson peak of glassy poly(vinyl chloride) was observed by Raman scattering [27], and not by neutron scattering [28], after plasticization by 10% of dioctyl phthalate. This meaningful difference between the Raman and neutron boson peak behaviours can be explained by the different origins of the Raman and neutron scattering excesses, as explained further below.

The observation of a correlation peak in PMMA/DBP demonstrates that the distribution of the plasticizer in PMMA is inhomogeneous: regions poor in DBP are separated by DBP-rich zones, and are arranged quasiperiodically. The neutron boson peak corresponds to the VDOS excess. From experiment, this inhomogeneous and quasiperiodic distribution of DBP in PMMA has no effect on either the position or the intensity of the VDOS excess, which is approximately determined by the sum of the VDOS of both components in PMMA/DBP [25]. Several informations can be deduced from this result. (1) As the boson peak is dependent on the intermolecular bonding, it is deduced that macromolecules of PMMA interact principally with other PMMA macromolecules. (2) The frequency of the boson peak depends on the correlation length- or heterogeneity size. Consequently, if the plasticization does not change the boson peak frequency, the correlation lengths in PMMA and DBP in PMMA/DBP are approximately the same as in pure PMMA and pure DBP.

As it is well known, the Raman boson peak intensity is proportional to the VDOS excess and to the frequency-dependent light-vibration coupling tensor $C_{\alpha\beta}(\nu)$. Therefore,

the enhancement of the Raman boson peak (Figure-2) comes from $C_{\alpha\beta}(\nu)$, which is expressed as follows for an isotropic material [29,30]:

$$C_{\alpha\beta}(\nu) \propto \int \int d\mathbf{r}_1 d\mathbf{r}_2 < \delta\chi_{\alpha\beta}(\mathbf{r}_1, \nu) \delta\chi_{\alpha\beta}(\mathbf{r}_2, \nu) > \quad (1)$$

α and β denote the polarizations of the exciting and scattered light respectively, $\delta\chi$ is the susceptibility fluctuation. Brackets denote the space correlation. $\delta\chi_{\alpha\beta}(\mathbf{r}, \nu)$ is proportional to the strain tensor $s_{\gamma\delta}(\mathbf{r}, \nu)$ corresponding to the vibrational mode of frequency ν [29,31]:

$$\delta\chi_{\alpha\beta}(\mathbf{r}, \nu) = P_{\alpha\beta\gamma\delta}(\mathbf{r}) s_{\gamma\delta}(\mathbf{r}, \nu) \quad (2)$$

$P_{\alpha\beta\gamma\delta}(\mathbf{r})$ is the elasto-optic tensor. The coupling coefficient $C_{\alpha\beta}(\nu)$ has two origins [29]: the elastic or mechanical fluctuations, which partially localize the vibrational modes, and the fluctuations of $P_{\alpha\beta\gamma\delta}(\mathbf{r})$:

$$P_{\alpha\beta\gamma\delta}(\mathbf{r}) = P_{\alpha\beta\gamma\delta} + \delta P_{\alpha\beta\gamma\delta}(\mathbf{r}) \quad (3)$$

The observation by SAXS of a correlation peak at a transfer momentum Q testifies the existence of periodic composition- or density-fluctuations [24]. Surely, these fluctuations induce periodic elasto-optic fluctuations $\delta P_{\alpha\beta\gamma\delta}(r)$ such that:

$$\delta P_{\alpha\beta\gamma\delta}(r) = \delta P_{\alpha\beta\gamma\delta}^0 \cos\left(\frac{2\pi a_\ell}{r}\right) + \text{harmonic terms} \quad (4)$$

with a_ℓ the period of PMMA/DBP observed by SAXS ($a_\ell = \frac{2\pi}{Q}$). The strain tensor in (2) is proportional to the space phase term $\exp(i\mathbf{k} \cdot \mathbf{r})$ of the corresponding acoustic vibrational mode. \mathbf{k} is the wavevector that characterizes the (non-necessarily propagating) mode. It is such that $k \simeq 2\pi\nu/v$, v being the sound velocity. From Equations 1 and 2, the contribution of the elasto-optic fluctuations to the light-vibration coupling coefficient will be maximum for $k = 2\pi/a_\ell$, i.e., for:

$$\nu \simeq \frac{v}{a_\ell} \quad (5)$$

In a pure non-plasticized PMMA glass no density fluctuations with a size larger than 0.5 nm are observed, so that it is expected that the mechanical fluctuations have a stronger contribution to $C(\nu)$ than the electric ones. Now, it was shown that the mechanical contribution to $C(\nu)$ presents no maximum and has a power-law frequency dependence [30,31]. Consequently, it was deduced that the Raman boson peak frequency is related to the neutron boson peak one, i.e., to the frequency of the VDOS excess. From different models [1,5]:

$$\nu \simeq \frac{v}{d_\ell} \quad (6)$$

d_ℓ being the correlation length or the heterogeneity size of glass. As the enhanced Raman boson peak of PMMA/DBP appears at a frequency close to that of pure PMMA (Figure-1), it is deduced that $a_\ell \simeq d_\ell$ and that the correlation of the elastic fluctuations in PMMA is not very different from that of the composition fluctuations in PMMA/DBP. In some way, the plasticizer “decorates” the elastic constant fluctuations. It is tempting to conclude that there are nearly periodic elastic constant arrangements in glasses, and that the boson peak corresponds to the Van Hove singularities of these periodic arrangements. As it will be emphasized in the following part, this explains the linear dispersion $\nu(Q)$ observed by inelastic X-ray scattering.

III. INELASTIC X-RAY SCATTERING AND HETEROGENEOUS NANOSTRUCTURE OF GLASSES. DISCUSSION

The linear dispersion of longitudinal acoustic excitations $\nu(Q)$, observed by inelastic X-ray scattering (IXS) in many glasses has been a subject of controversy. While some authors [20–22] observed the linear dispersion up to frequencies higher than that of the boson peak ν_b , others claimed that the dispersion linearity stops at a frequency lower than ν_b , at least in the case of silica glass [32]. It is indeed surprising to observe propagating modes, at frequencies higher than ν_b , since acoustic phonon attenuation measurements in silica [33] and PMMA [34] showed that propagation ceases at frequencies lower than ν_b . Recently it was shown that the linear dispersion observed in the region of boson peak can be explained by non-propagating modes in an elastically heterogeneous structure [23]. This interpretation is now simply described in relation to the previous part.

The static structure factor of glasses, as observed by SAXS, shows no feature indicating the presence of nanoheterogeneities with a size larger than 0.5 nm. As emphasized above, this non-observation is in agreement with the absence of contrasted density nanoheterogeneities but not in disagreement with the presence of elastic constant ones. As already suggested, the plasticizer highlights the elastic constant nanoheterogeneities like it does in semicrystalline polymers [35]. The broad correlation peak, that is observed by SAXS with PMMA/DBP [24], indicates (1) that at the nanometric scale there is a distribution of periods and (2) that the periodicities are extended on relatively short distances. What is observed by the IXS of a glass? In the spectral range of the boson peak, IXS simply probes the dynamic structure factor of the vibrating nanometric structure. In the network submitted to a vibration, whose wavelength is close to the heterogeneity size, the elastic periodicity is transformed into a density periodicity so that a dynamic correlation peak is observed. From (6) and $a_\ell \simeq d_\ell$, the dispersion relation $\omega \simeq vQ$ ($\omega = 2\pi\nu$) is obtained. The linearity can be observed in the whole spectral range of the boson peak because of the above mentioned period- or size heterogeneity- distribution. By scanning in frequency ν or in transfer momentum Q , one scans the size distribution.

Following this interpretation, the observed IXS peaks correspond to the modes at the edge of the Brillouin zones or at the Van Hove singularities of nearly periodic arrangements comprising several elastic constant heterogeneities. Consequently, the observed linear dispersion in the spectral range of the boson peak does not correspond to the dispersion curve in a single periodic or continuous network. Furthermore, these modes observed by IXS do not propagate phonons (group velocity equal to zero at the edge of Brillouin zone), in agreement with other measurements [33,34]. Finally, it is noted that this interpretation is not in contradiction, on the one hand, with the topological origin of the Q^2 -dependence of the vibration attenuation [20,21,36] and, on the other hand, with numerical simulations which seem to confirm the linear dispersion and the Q^2 -dependence of the attenuation [37,38].

IV. CONCLUSION

The boson peaks observed by Raman and neutron scatterings and the Brillouin peak observed by inelastic X-ray scattering in the nm^{-1} transfer momentum range are in agreement

with the nanometric cohesion heterogeneity of glasses. The enhancement of the Raman boson peak in plasticized PMMA compared to that in pure PMMA and the non-enhancement of the neutron boson peak suggest that the plasticizer highlights the cohesion heterogeneities by density or composition ones and, consequently, by elasto-optic constant heterogeneities. On the other hand, these observations and the relatively broad correlation peak observed by small angle X-ray scattering in plasticized PMMA show that the density heterogeneities, and consequently the cohesion ones in pure glass, form periodic arrangements. Such a topological nanostructure possibly explains the linear dispersion observed by inelastic scattering: the peaks, that are observed in the spectral range of the boson peak, can correspond to the Van Hove singularities of the nearly periodic arrangements.

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FIGURES

FIG. 1. Reduced Raman spectrum of PMMA/DBP at $T=140$ K (full circles), compared to the addition of the spectra of pure PMMA and DBP at the same temperature (open circles). The inset shows the reduced Raman spectrum of DBP at 140 K.

FIG. 2. Vibrational density of states divided by the square of frequency, $G(\nu)/\nu^2$, deduced from the inelastic neutron scattering at 30 K. PMMA: empty circles; PMMA/DBP, experiment: full squares; calculated: empty squares; DBP: full circles. The normalization is obtained by an arbitrary equalization of $G(\nu)/\nu^2$ at 1 THz.



